

Magnetism and Superconductivity: The Simple Approach (update)

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Free Electron gas

First consider the free electron gas in an homogeneous magnetic field. For motion transverse to the magnetic field, one obtains Landau energy levels at

$$E_n = \left(n + \frac{1}{2}\right) m_B B$$

where m_B is the Bohr magneton.

Of thermodynamic relevance is the energy density.

The energy density for motion parallel to the magnetic field is unaffected. For a given electron density, with increasing magnetic field, the passing of the Fermi energy through the discrete Landau levels will lead to a temperature-dependent oscillation (Schubnikov- de Haas osc.). We ignore this oscillation and take the continuous limit of the energy density. It turns out that this gives exactly the same energy density as the field-free case, except that it starts at the energy

$$E_0 = \frac{1}{2} m_B B$$

above "ground zero".

That means, that the chemical potential in a magnetic field B is given by

$$\mu = \mu_0(T) + \frac{1}{2} m_B B$$

The Gibbs Free Enthalpy of the electrons is

$$G = N \mu = V n \mu \quad (n \text{ is the number density per volume } V)$$

and the magnetisation is given by

$$\frac{\partial G}{\partial H_T} = -VM = -Vn \frac{\partial \mu}{\partial H_T}$$

If we took naively the field B for the external Field H , we would obtain a magnetisation

$$M_s = -\frac{1}{2} m_B n$$

that is a magnetisation opposite to the external field, finite at zero external field (!), of huge strength. For metallic electron densities n one obtains fields of the order of 1 Tesla.

Before we go on, let us make a remark on our neglect of spin magnetisation.

Spin effects are proportional to the difference between the numbers of spins up and down. The effect we are treating is proportional to the entire density, hence the sum of numbers of spin up and down. The relative importance of spin to the "energy shift" effect will then be

$$\frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}} \quad \text{hence completely unimportant.}$$

The correct treatment of the magnetisation is

$$\mu = \mu_0(T) + \frac{1}{2} m_B B = \mu_0(T) + \frac{1}{2} m_B (H + M) = \mu_0(T) + \frac{1}{2} m_B \left(H - n \frac{\partial \mu}{\partial H_T} \right)$$

with the solution

$$M(H) = M_s (e^{-H/M_s} - 1)$$

The magnetisation is zero at $H=0$ and tends towards the saturation magnetisation M_s , always negative, hence opposite to the external field H . The slope at $H=0$ is -1, which is perfect diamagnetism at that point.

Free hole gas

What applies to the free electron gas (n-band) also applies to a p-type hole gas, as long as the Fermi energy is well in the parabolic dispersion region. Everything is the same except that energies are negative. That means that the energy density with magnetic field is the same as without a field and *lowered* by

$$E_0 = -\frac{1}{2} m_B B$$

Ignoring the low-energy band structure and assuming that one can continue the inverted parabola, the change in the chemical potential is

$$\mu = \mu_0(T) - \frac{1}{2} m_B B$$

The magnetisation is then

$$M_S = \frac{1}{2} m_B n$$

for all values of H and independent of temperature. This is spontaneous magnetisation, a candidate for ferromagnetism. For Iron, one obtains 1.5 Tesla with this formula. If the hole effect is responsible for ferromagnetism, the Hall coefficient of those metals should correspond to positive charges.

Of course, a band has finite energy extension, with parabolic dispersion at the lower and upper end. Hence, in a magnetic field, the bottom is lifted up and the top is lowered, whereas the belly bulges out to accommodate the total number of states which remains unchanged. As the temperature rises, holes invade the band and the finite energy range comes in to lower the magnetic response.

This is valid for any band, n or p type.

"Real" Metals

Most metals have weak magnetic response and always a temperature dependence.

One can invoke

- half-filling of bands where at some point of filling, magnetisation ceases. This might be the case for simple metals (Alkali, Erdalkali)
- simultaneous presence of n and p-type bands where the n-bands are lifted, the p-bands lowered by a magnetic field to keep the chemical potential unchanged and, thus, the magnetisation low or null.
- excitation from p-bands into n-bands with diamagnetic response lowering the para/ferromagnetic p-reponse (Curie-law)
- finite band-energy-width, as already mentioned, lowering the magnetic response with temperature.
- bands off-center from the Γ -point of the Brillouin zone; a uniform field will look like a periodic field from their vantage point and thus produce weak response.

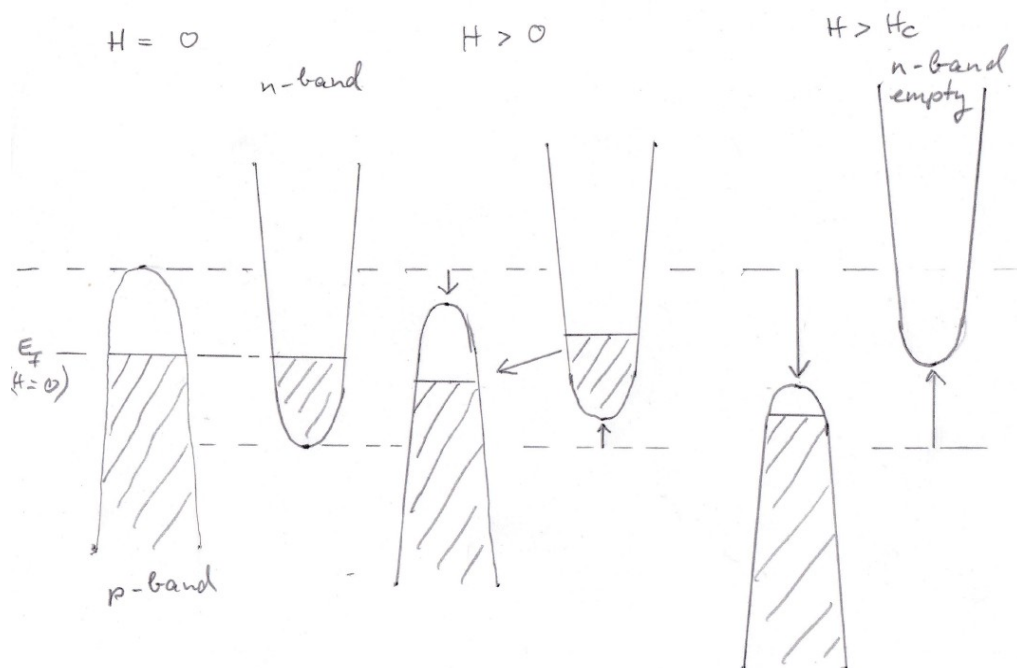
Antiferromagnetism

Let us look specifically at the case of a p-band at the Γ -point and an off-center n-band at the Fermi energy. (Drawing) When we turn the magnetic field on, the p-band is lowered as described above. Primitively, this gives a uniform (para/ferro)magnetisation

The n-band sees a periodic magnetic field and will produce a periodic diamagnetic response. But this is seen from the vantage point of the n-band. In real space, one obtains a two-fold response, a uniform diamagnetic response and a periodic modulation of the uniform p-band magnetisation.

There will be paramagnetic response at low field because lowering of the p-band is a first order effect whereas the lifting of the n-band is higher order due to the effective "periodic" nature of the field.

As the field increases, the n-band flows out into the p-band and, once empty, we are left with the ferromagnetic response of the p-band. (drawing)



This can describe Antiferromagnetism.

Note on Exchange Interaction

"Exchange Interaction" simply does not exist. It is a misunderstanding of the anti-symmetry of the fermion wavefunction. When we have two electrons with aligned spins, only antisymmetric relative spatial wavefunctions are possible. When we have two electrons with opposing spins, all relative spatial wavefunctions and symmetries are possible. In the case of an antisymmetric spatial wavefunction, the total wavefunction for opposite spins takes the form

$|\Psi\rangle = f(r_1, r_2)(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle)$ where the spin part is symmetric to retain overall antisymmetry.

Hund's Rule

If spin alignment does not provide an energetic advantage, the increased entropy of spin multiplicity would still favor aligned spin configurations in atoms. There is, however, an energetic advantage of aligned spins in atoms due to electron-nucleus LS-interaction. In an atom, the electrons form a lattice-like structure to minimize mutual Coulomb energy. Such a "Coulomb lattice" is possible for point charges in a lower (1,2) dimension. This "lattice" circles the nucleus in a stochastic fashion, but the electrons are in lockstep relative to each other. Two electrons opposite the nucleus circle then in the same direction and the LS-interaction will align their two spins in the same sense. Hence, spin alignment has an energetic and an entropic advantage and leads to Hund's rule for atomic ground states.

Superconductivity

Thermodynamic Currents

Thermodynamic Currents (TC) are macroscopic currents that contribute to the H-magnetic field.

When they exist in a sample in thermodynamic equilibrium, they have to satisfy the conditions

- the chemical potential of the current carriers, the electrons of course, must be everywhere the same
- a lowering of the TC leads to an increase of the system's free enthalpy (Gibbs potential)

TCs have a curious property: they must be kick-started, either by an electromotive force (EMF) or by an external current source. The reason is that there is no mechanism that installs a TC, even if this would bring the Gibbs potential to an absolute minimum.

As an illustration, let's make an experiment (drawing).

Take a superconducting, hollow tube-ring through which we pass a current-carrying wire.

Consider the cases

1a) Start out at temperature $T > T_c$ with a central finite current $I_c(0)$

Cool down below T_c while maintaining the central current. The ring will diamagnetically shield the central current and reproduce the central current's magnetic field on the outside of the ring.

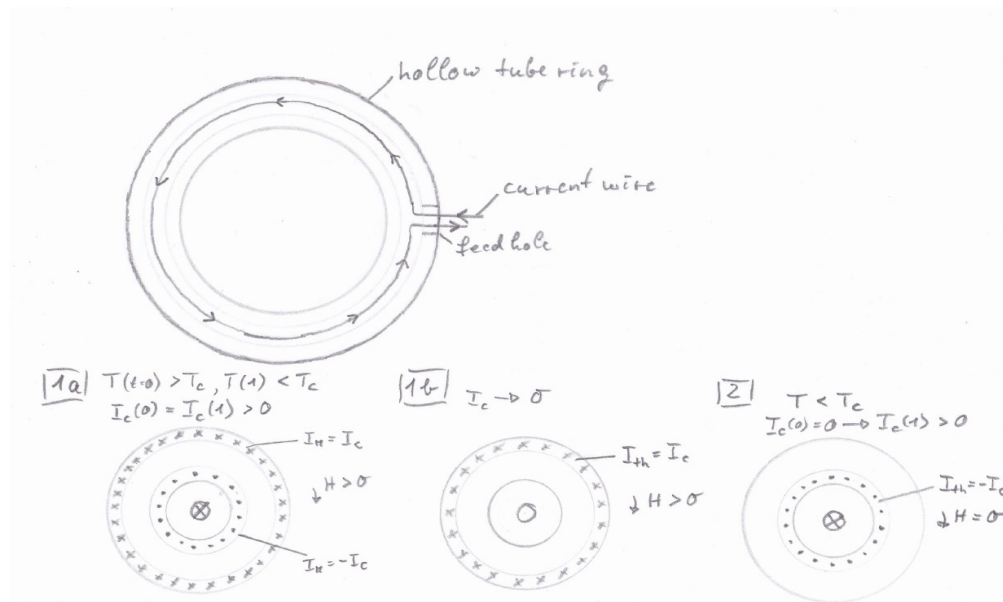
1b) Now turn the central current off.

The EMF will start a thermodynamic current which we would primitively assume to take the place of the outside magnetisation current (drawing). We will see below that this is not entirely the case, but we will get a thermodynamic ring current anyway.

2) At temperature $T < T_c$ and zero central current, turn the current on.

The EMF starts a countercurrent on the inner perimeter of the tube that shields the central current and the magnetic field on the outside of the ring is zero.

Incidentally, this is the case of lowest G in the presence of a central current, but this was not obtained in the case 1a.



Superconducting Iron (?)

Let us take the case of a straight ferromagnetic soft iron tube which has been magnetised by a forward current such that its magnetisation is entirely azimuthal in the direction of the magnetic field of the forward current. Such a tube has no external magnetic field but must be carefully shielded from external field to not destroy this configuration.

The contributions to the Gibbs potential are

- the kinetic energy of the currents, for which we take the London Ansatz
- the magnetic field energy, in all space
- the electric field energy due to the inhomogeneity of the magnetic field
- the magnetisation energy

As we have seen, the magnetic field affects the chemical potential, leading to the outflux (influx) of electrons from (to) regions of higher (lower) chemical potential. This leads to the formation of a space-charge which creates an electric field in the sample whose energy must be added to the energies already present.

The magnetisation energy of a ferromagnet is the only negative quantity around

The total Gibbs potential takes the form

$$G = G_0 + \int dV_s \frac{1}{2} d^2 (\nabla \times H)^2 - \int dV_s M H(R) + \int dV_{tot} \frac{1}{2} H^2(R) + \int dV_s \frac{1}{2} E^2 (\partial H / \partial R(R))$$

The volume integrals over the magnetisation and electric part are over the sample volume, since total charge is zero. The magnetic field energy extends over the entire space and is sensitive to the presence of other currents and magnetisable matter, which we ignore for the moment.

In order to close the system of equations, we have to determine the relation between electric field and magnetic field variation.

The electric field just has to counter the magnetic-field induced gradient of the electron chemical potential and for our ferromagnet we get

$$eE = -\nabla \mu(H) = m_B \frac{\partial H}{\partial R}$$

more generally

$$eE = -\nabla \mu(H) = \frac{-\partial \mu}{\partial H} \nabla H$$

Here, we have to use the Bohr magneton. In the volume integral, we have to multiply with the particle density which gives $n m_B = M$, the magnetisation.

d is the London length. The electric field contribution implies a similar length \hbar/mc , which is of the order of a picometer. Current and electric field terms have the same functional form, both contain derivatives, and the squares of their lengths add up. The London lengths are of order of several hundred Angstroms, hence dominant.

In order to eliminate a positive magnetic field contribution from outer space, let us take our magnetised tube and put it in an outer tube which carries the return current. This way, there is no external magnetic field and the integral extends only over the sample volume.

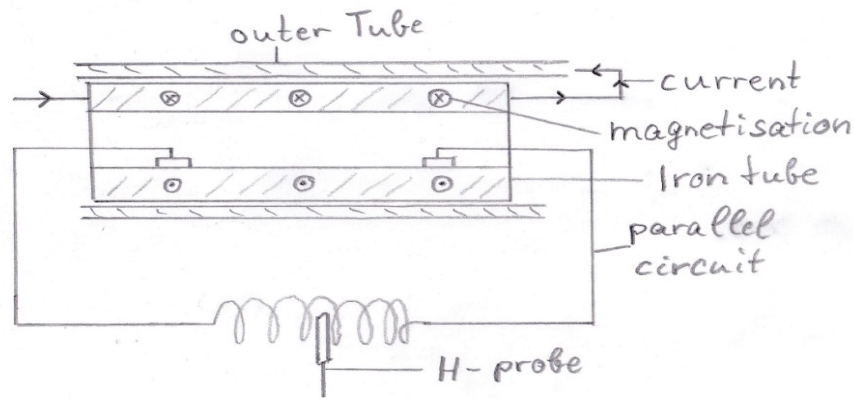
The solution is approximately $H(r) = H_I (1 - \exp(-(\frac{r-r_0}{\lambda})))$ r_0 is the tube inner diameter, H_I is the amplitude given by the external current I .

The current flows only in a thin layer around the inner diameter.

To measure the absence of resistance, one connects a parallel wire from the tube inside which one winds into a coil. Magnetic measurement of the coil reveals the presence of a current, hence resistance. Zero coil magnetic field means no resistance in the iron.

I underline that all components have to be shielded from external fields. (drawing)

The TC flows in a thin surface layer. In normal iron, we have domain formation to minimize the external field. These domains are at the surface and render TCs impossible. This should explain why superconductivity has not yet been observed in iron.



Superconductivity in any Metals

The magnetic field energy that appears in the Gibbs potential, as already mentioned, extends over the entire space and is sensitive to the presence of other currents and magnetisable matter. That means that one might induce TCs in metals that are not superconducting and at any temperature. In particular, consider a tube inside another tube which carries a current with an independent current supply that is current-stabilised. H_i , H_{ex} are the internal and external field contributions, respectively. We suppose that the TC, if any, is going counter to the outer-tube current. The Gibbs potential then takes the form

$$G = G_0 + \int dV_s \frac{1}{2} d^2(\nabla \times H)^2 + \int dV_{tot} \frac{1}{2} H_i^2 - \int dV_{tot} H_i H_{ex} + \int dV_s \frac{1}{2} E^2$$

The volume integral outside the sample now provides a *negative* magnetic field contribution. But there is more: This negative term extends over all external space and scales with the tube length. That means that the magnetic energy per unit length increases with the total length. This is due to the $1/r$ behaviour of the magnetic field for the infinitely long, straight wire.

And that means that we can always find a way to make a TC in the opposite sense profitable to the inner tube, whether it be superconducting or not. It need not even be magnetisable, least of all diamagnetic. *Any metal can superconduct if hit hard enough.*

Diamagnetic Superconductors

One has to wonder why a strong diamagnet such as a superconductor should hold any thermodynamic current at all, least of all be particularly known for it.

When we look at the above Gibbs potential, we could throw out all the negative terms and still get a solution to the Lagrange equation which would be of no physical reality because a TC needs an incentive, plus it must be kick-started.

Quantitatively, let's consider the Gibbs potential of the perfect diamagnet

$$G = G_0 + \int dV_s \frac{1}{2} \lambda^2 (\nabla \times H)^2 + \int dV_s \frac{1}{2} H_{TC}^2 + \int dV_s \frac{1}{2} H_{TC}^2 + \int dV_{ex} \frac{1}{2} (H_{TC} + H_M)^2 + \int dV_s \frac{1}{2} E^2$$

It contains the magnetic energy of the TC twice: the second part is the energy needed for the diamagnetic screening currents. It can't get any worse.

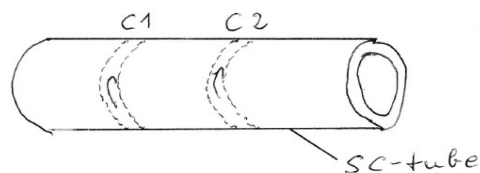
The screening currents due to diamagnetic magnetisation, additionally to the TC contribute to the external magnetic field energy, where $B=H$ and $M=0$.

But, why should a current circulate in a loop when the sample's free enthalpie is lower without?

The reason for this is the same as for any metal: it superconducts because it shields another current.

With that in mind, let us look at the superconducting current loop. If the TC flowed in a circular outside layer, as we (incorrectly) pictured above, there would be no advantage to have a TC and there would be no mechanism that could resist a lowering of the TC.

Look now at a SC-tube. Suppose a localised current (C1) somewhere around the tube. Suppose a second localised current (C2), parallel to C1 and in the same direction (drawing).



When the two currents approach each other, more of their flux will penetrate into the diamagnetic SC-tube outside the currents and raise the free enthalpy.

When the two currents increase their distance, less flux will penetrate in the outside region but flux extinction between the two currents will weaken and thus also increase free enthalpy.

Hence, there will be some optimum distance between the two currents which one can determine by precise mapping of the tube's magnetic field.

If single electrons are the current carriers, our minimum flux quantum therefore must have double electron charge.

The phenomenological consideration of two currents stabilising each other means, that the *fluctuations* of one current get coupled to the *fluctuations* of the other current. On the elementary level this is tantamount to the creation of *two-particle quasiparticles* (2PQ).

These 2PQ are long-range in nature and need not even belong to the same material. In a strongly diamagnetic material, we expect the presence of these 2PQ also in thermal equilibrium and across material bounds.

Flux quantisation is achieved by the requirement that the angular momentum of this two-particle system be quantised in units of $\hbar/2\pi$.

Angular momentum is defined as

$$\vec{L} = \vec{r} \times \vec{p}$$

\vec{p} is the momentum which can be written, in suitable gauge, for charged particles as

$$\vec{p} = \frac{q}{c} \vec{A}$$

A is the vectorpotential, q is the total charge, Φ is the magnetic flux through the loop. In absolute values we get, taking into account the quantisation condition

$$L = \frac{q}{2\pi c} \oint \vec{r} \cdot d\vec{r} = \frac{q}{2\pi c} \oint dr A = \frac{q}{2\pi c} \Phi = \frac{n\hbar}{2\pi}$$

$$\Phi = \frac{n\hbar c}{q} = \frac{n\hbar c}{2e}$$

This is the customary observed flux quantisation.

One notes that the angular momentum of the magnetic flux makes the tube a "spinning" top. This is true for any magnetic bar but the dynamical effect (precession) is so weak as to be virtually undetectable.

"Normal" Superconductivity

The Isotope Effect suggests an implication of phonons in the realisation of the superconducting state (SC). When phonons make transitions between electron states within one band, all we get is some polaron-like band distortion, but no qualitative change.

But phonons can connect two bands, at different places in the Brillouin zone. For this, they have to match the wavevector difference between bands, hence the need for short-wavelength phonons.

They also have to match the energy difference where resonance only occurs at the phonon energy.

This energy is small compared to electron energies which means that we are only dealing with the portions of bands that overlap energetically.

If phonons succeed in binding electrons through this mechanism, they create a band of their own which is made up from the electron states withdrawn from the preexisting bands involved.

Let us look specifically at the phonon-connection of a p and an n-band.

In the overlap, at given energy, state numbers in each band do not match and only the minority band is extinguished to enter the "condensate".

Simultaneous band extinction occurs only in the narrow range of the phonon energies. We then get a "band gap" from zero to a small value. (drawing)

The phonon Hamiltonian responsible for this p-n-band coupling has terms

$$Qa_{np}^+$$

which is the destruction of an electron in the p-band and the creation of an electron in the n-band.

But the destruction of a p-electron is tantamount to the creation of a hole, hence

$$Qa_{np}^+ = Qa_{nh}^+a_h^+$$

That is the creation of an electron-hole pair which I will refer to now as a "holelectron".

Let us look at its spin: the destruction of a spin-up state in the p-band corresponds to the creation of a spin-down hole, hence

$$Qa_{n\uparrow}^+a_{h\downarrow}^+$$

our holelectron has zero total spin.

It also has zero total charge, due to its simultaneous n and p character.

Let us be very clear: phonons bind *single electrons*. We are *not* talking about binding electrons together. We are dealing entirely with a *single-particle hamiltonian*.

The zero-charge character of the holelectron gives us two avenues for creating bound states

- phonons can bind the electron in their fluctuating, periodic field
- electron-hole correlation can reduce the Coulomb energy with respect to the Coulomb energy of the n or p electron. As long as the electron evolves in one band or the other, its fluctuating electric field energy will depend on its charge. When correlated, these fluctuations reduce or even cancel each other due to the effective opposite charge of each constituent. This, of course, reflects the zero-charge character of the holelectron.

Depending on which mechanism the low-energy state formation primarily depends, we get

- maximum Isotope Effect for the phonon binding
- reduced Isotope Effect for Coulomb energy reduction

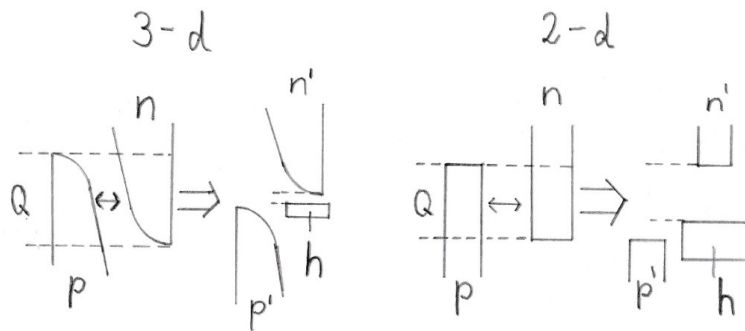
In the latter case, the phonon participation reduces to matching the wavevectors of the n-p states.

Dimensionality plays an important role. In 3 dimensions, we get a square-root energy density from the band top/bottom with a majority-minority band at each energy, as already mentioned.

In 2 dimensions, superconducting planes, energy density is constant and, if it happens to be the same for n and p band, band extinction extends over the whole energetic overlap to produce a comparably huge band gap.

Consequently, the number of condensate states is equally great.

(see drawing)



It is number and energy of the holeelectron states, the "condensate", that determine the lowering of the chemical potential.

When we turn on a magnetic field, the p and n bands will behave as we already discussed in the section on Antiferromagnetism (AF): the p -band goes down, the n -band goes up, thus reducing the overlap and the number of holeelectron states.

This, in turn, raises the chemical potential and produces the diamagnetism observed.

The holeelectrons, having charge zero, are unlikely carriers of an electric current. They actually aren't. Their only role is to produce the mechanism for strong diamagnetism.

The Fermi energy will cross through the p -band and holes, singly charged, will be the current carriers. This is kind of ironic since a free holegas produces ferromagnetism, but we see here, that the individual nature of particle dynamics have no meaning and must be subordinated to the collective thermodynamic situation.

Let us now consider specifically, the p -band at the Γ -point and the n -band off-center. Once again, we already had this situation for Antiferromagnetism. When we immerse a sample into a magnetic field, we get the formation of regions of field penetration. There, SC has ceased, meaning that the magnetic field has shifted n - p -bands such that the overlap has become negligible and the n -band has emptied itself into the p -band. The region of flux penetration has become *ferromagnetic*.

The flux region in the external field is a bar magnet. But we know, that bar magnets cannot exist without constraining forces. If we split an iron bar magnet along the field lines, it will speed apart to reduce the magnetic energy (if it can't flip over). This is a volume effect.

Likewise, the regions of flux penetration will split up into tiny flux tubes until the surface to volume ratio has increased so much that the inevitably positive surface energy puts a stop to further reduction.

The resulting flux tubes are bar magnets that arrange in a closest packing (hexagonal) to maximise mutual distance. The sample, fully magnetised, will be a Ferromagnet (*not* a paramagnet).

We recognise, of course, the phenomenology of Type II SC.

Type I SC must have off-center n - p -band interaction. In the fully magnetised state they are presumably slightly paramagnetic. We might also get the curiosity of a completely filled p -band, hence no magnetisation at all and electrical insulation.

Flux penetration does not minimize the length of NC-SC interface. Instead of round discs, we get flux stripes. This already annuls interface curvature, apparently a source of energy, and also reduces magnetic energy due to paramagnetic magnetisation. One has to look at the experimental values of their paramagnetism to draw any further conclusions.

Type II - Type I Reentrant Superconductors

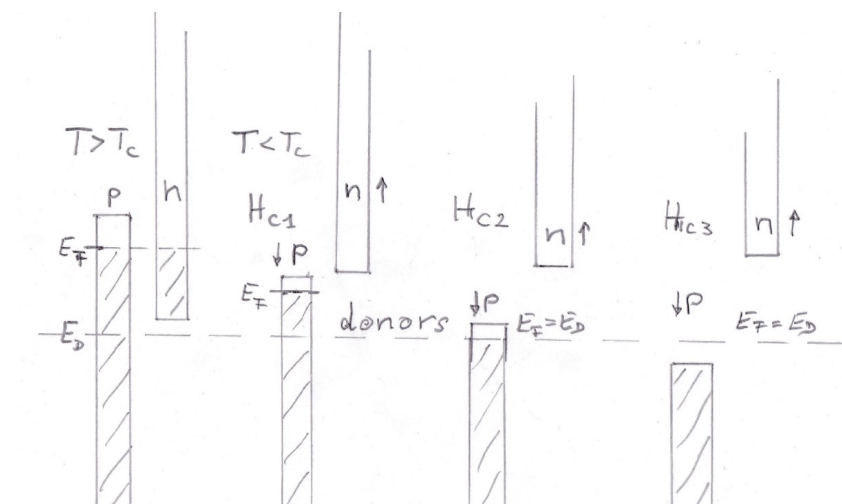
Consider a type II SC with a p-band at the Γ -point and an off-center n-band *plus* donor impurities (n-type) below the n-band. (drawing)

When we turn on a magnetic field, we reach a first critical field where superconductivity ceases. We are left with an n-band that has emptied itself into the p-band. The donor energy level is unaffected by the magnetic field

The Fermi level is still above the donor level, the sample is ferromagnetic and forms flux tubes as already explained.

Upon increasing the magnetic field, we reach a second critical field when the p-band has been so much depressed that the Fermi level reaches the donor energy. The donor impurities act as a buffer that fixes the Fermi level which becomes insensitive to magnetic field. Hence, magnetisation drops to zero and the type II flux tube behaviour cedes to type I flux stripes behaviour. The sample is still electrically conducting at this stage.

Upon further increase of the magnetic field, we reach a third critical field, the last one, when the p-band top passes under the donor level. The donors, if sufficiently numerous, fill the p-band. The sample is now an electrical insulator.



Future Superconductors

Diamagnetism is the name of the game and the question of how to produce SC for everyday purposes is how to make conducting diamagnetic substances. One route is to design them from scratch, a challenge for solid-state chemists. The other is the observation, that we do not need holecarriers or other fancy constructs, but just an n-band filled only in the parabolic dispersion regime. For this, let's take a simple metal like the Alkalies which have n-bands half-filled.

If we find a way of reducing their valency by adjoining suitable materials, maybe halogenes, we have a chance to obtain perfect diamagnets quite readily.